SVETOMIR Ž. MILOJEVIĆ[1]
SANDRA B. GLIŠIĆ[2]
DEJAN U. SKALA[2]

[1]Faculty of Tehnical Sciences, Kosovska Mitrovica, Serbia
[2]Departement of Organic chemical technology, Faculty of Technology and Metallurgy, University of Belgrade, Belgrade, Serbia

THE BATCH FRACTIONATION OF *Juniperus communis* L. ESSENTIAL OIL: EXPERIMENTAL STUDY, MATHEMATICAL SIMULATION AND PROCESS ECONOMY

The separation in a batch vacuum column of the essential oil of common juniper berries (Juniperus communis L., from the southern part of Serbia) was analyzed. The main goal of the analyzed separation process was to isolate several fractions from the essential oil which mainly contained α-pinene, sabinene and myrcene. These compounds contain about 65 mass% of the essential oil produced by hydrodistillation from the juniper berries originated from the southern part of Serbia. The results of experimental work in a laboratory column with 36 theoretical stages under vacuum (8.0-3.35 kPa) was simulated using Aspen software, and a proposed mathematical model was used to analyze some other operating conditions for fractionation of juniper berry's oil (number of plates: 25, 36 and 45 and reflux ratio: 2-10). According to the results of performed simulations, the most acceptable separation procedure which takes into account the prices of raw materials and distillate (α-pinene) as well as consumed energy was proposed.

Key words: vacuum fractionation; Juniper communis L.; α-pinene, Aspen simulation.

The essential oil of juniper berries is one of most valuable bioactive and commercial product. The content of juniper essential oil differs depending on its origin and the amount of some components may significantly vary [1,2] which highly influence the fractionation process as well as the composition of the obtained products. In the studies of the essential oil of juniper fruit, it was established that the pharmacological features are derived from its constituents. All terpene hydrocarbons are antiseptic, anti-inflammatory, antibacterial, pain-killers, sedatives, stimulators and media for the excommunication of excrete mucus [3-5]. α-Pinene is certainly an acute antiseptic and it was found to act as a rubefaciens [3]. Sabinene has pronounced anti-inflammatory and antibacterial properties [3]. Myrcene acts as a sedative, an anti-inflammatory agent and as a pain-killer for peripheral organs [3] and stimulates the recovery of the liver [4]. Limonene is known for its strong antiviral properties, helps detoxify the liver, abstracts carcinogenic substances and can retard a tumor development [4]. Reports regarding the essential oil from juniper berry can be found in the literature. In the previous published study [1,5] it was shown that bioactive components from the juniper essential oil, especially α-pinene and sabinene possess a high inhibitory activity against many micro-organisms with the small minimum inhibitory concentration (MIC) values [1,6-8].

In the literature, there are several works reporting the vacuum fractionation of the essential oil, mainly deterpenation of citrus oils [9-11]. Deterpenation of bergamot oil was performed in the 15 cm long column (without any data on the number of stages) at the pressure of 350-400 Pa and it was found that the vacuum distillation was very effective in removing monoterpenes from bergamot oil [9]. However, the separation of oxygenated compounds from non-volatile compounds was not satisfactory due to higher operation temperatures [9]. The recovery of monoterpenes is very good (only 1 mass% remain in the residue) while the recovery of oxygenated compounds is generally lower than 70% [9]. This could explain the increase of the viscosity of the residual in the vessel with decreasing the content of the highly volatile components; consequently, mass and heat transfers become more difficult. Also, Lopes and co-authors fractionated sweet orange oils in a vacuum distillation column (1.30 m height, 15 mm i.d.) packed with Raschig rings at 80 °C, from 10-30 mbar and with a reflux ratio

in the range of 0.25-0.75 [10]. They found that the best operation conditions for preparing folded oils were obtained at 20 and 10 mbar, the products contained the lowest terpene hydrocarbon fraction and the highest oxygenated fraction [10]. Nowdays, there is no data about vacuum fractionation of juniper berries' essential oil reported in literature.

The aim of this study was focused on the separation of α-pinene, using the fractional vacuum distillation. Based on experimental investigation, the simulation of batch vacuum fractionation using Aspen software was also performed with the aim to confirm the simulation procedure which might be used for further process optimization.

One problem in realizing the simulation by using the Aspen software is in a fact that although used software contains an excellent bank of physical and thermodynamic parameters there is still the lack of some data necessary for calculation (*e.g.* the vapour pressure data for the essential oil's components). These data were calculated by using the method proposed and recommended in literature. The result of the performed simulation and its good agreement with experimental data confirmed the used simulation method, the specified thermodynamic model, and the physical and thermodynamic parameters of the components. According to the results of simulation the optimal operating conditions (number of plates, and constant reflux) for fractionation of juniper berries' oil was determined satisfying the goal to produce defined fraction of pure α-pinene followed with most acceptable economy.

EXPERIMENTAL

Plant materials

Purplish-blue juniper berries were collected at the end of September 2002 from Leposavić, the south side of Kopaonik, Zubin Potok and the Mokra Gora Mountian and voucher specimens (16036 BEOU; Snežana Vukojčić) were deposited at the Herbarium of the Institute of Botany and Botanical Garden Jevremovac, Faculty of Biology, University of Belgrade. The berries were air-dried at room temperature. They were stored in double-layered paper bags at ambient temperature, protected from light and well air-conditioned in order to prevent fermentation. Hydrodistillation was conducted by a standard procedure (Clevenger apparatus) with juniper berries which had previously been chopped in a domestic blender. The yield of the obtained essential oil was about 1.15 wt%.

Fractionation

Batch vacuum distillation was performed in a distillation column shown in Figure 1. The column is

29 mm inner diameter and 2 m high and packed with NORMAG type A packaging. The column has 36 theoretical stages that were determined experimentally by the standard mixture of CCl_4-C_6H_6 using the procedure previously reported [12]. Fractionation of the essential oil was conducted at absolute pressures of 8.0 and 3.35 kPa with a reflux ratio of 5. Fractions of approximately 10 cm^3 were collected during the fractional distillation and analyzed using GC-FID and GC-MS.
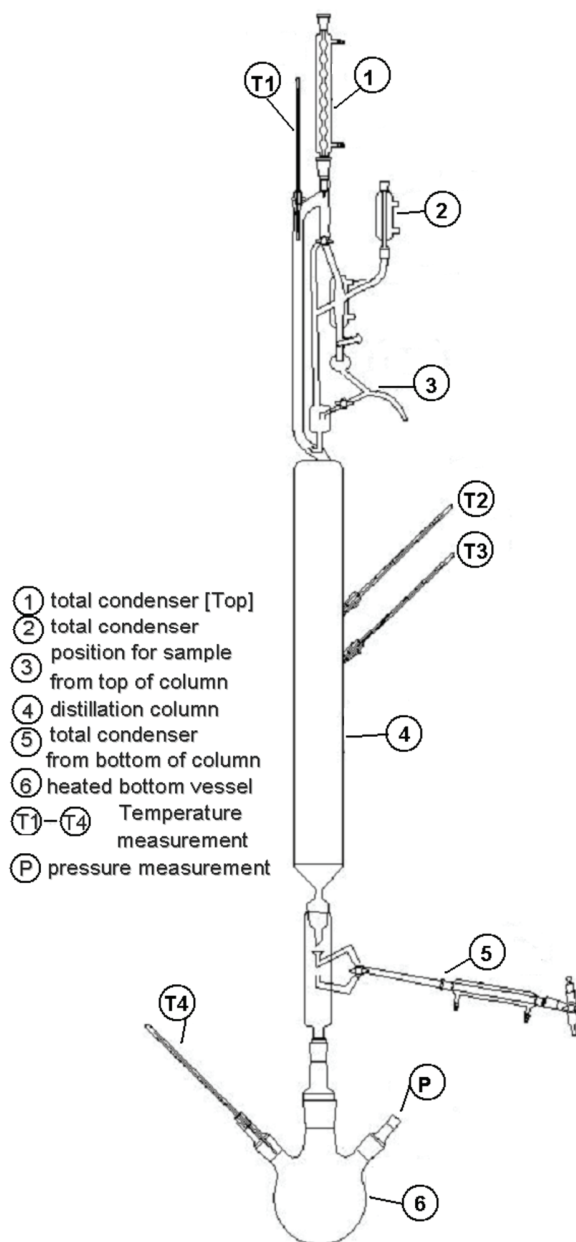
Figure 1. Schematic draw of the column for distillation (rectification column).

① total condenser [Top]
② total condenser
③ position for sample from top of column
④ distillation column
⑤ total condenser from bottom of column
⑥ heated bottom vessel
T1–T4 Temperature measurement
P pressure measurement

GC-FID Analysis

The samples collected during batch distillation were dissolved in *n*-hexane and analyzed by GC-FID

(Varian 3400). A fused silica DB-5 capillary column, 25 m×0.32 mm internal diameter, and 0.25 μm film thicknesses, was used. The purged splitless mode of sampling was implemented. The column temperature was maintained at 50 °C for 2 min and then programmed to increase as follows: at 2 °C/min to 250 °C, and holding at 250 °C for 5 min. The flow rate of the carrier gas (nitrogen) through the column was 2 mL min^{-1} and the inlet pressure was 68 kPa. The injector temperature was 250 °C and the detector temperature 300 °C. The quantitative presence of a compound in the samples was determined using the method of peak-area normalization, without the application of response factor corrections. Injections were repeated in triplicate.

GC-MS Analysis

The samples prepared using the same procedure as for the GC analysis were subjected to GC-MS analysis on a Varian 3400 split/splitless (1:20) gas chromatograph with a mass spectrometry detector Finningan Ion Trap ITD-705, ionization voltage of 70 eV. A fused silica Supelco column PTE-5, 30 m×0.25 mm internal diameter and 0.25 μm film thickness was used. The column temperature was maintained at 60 °C for 1 min and then programmed to increase as follows: at 4.3 °C/min to 286 °C and holding at 286 °C for 5 min. The linear flow velocity of the carrier gas (hydrogen) through the column was 1 mL min^{-1}. The injector and detector temperature were 250 and 300 °C, respectively. The sample (1 μL) was injected in the split mode (1:60).

The identification of the main compounds present in the essential was based on the comparison of their retention time and GC elution sequence with literature data for juniper berry essential oil [13-15] and also by matching the mass spectra of every GC peak with those of the AMDIS program, ver. 2.1. The composition of the juniper berry essential oil used for fractionation is shown in Table 1.

RESULTS AND DISCUSSION

The experimental vacuum fractionation

The batch vacuum fractionation of juniper berries' essential oil was performed in a distillation column which contains 36 theoretical stages. The other operating conditions were: hold-up per stage: 0.001 kg, condenser hold-up: 0.005 kg, condenser pressure: 7.3 kPa, column pressure drop: 0.7 kPa, boil-up rate 0.0339 kg/h at total reflux and boil-up rate 0.0249 kg/h at reflux 5. The detailed operating procedure (temperature on the top and bottom, time of fraction accumulation and their masses) and masses of collected fractions are given in Table 2.

As it could be seen from Table 1, the juniper berries' essential oil is rich in α-pinene and with sabinene and myrcene (about 72 mass% of the oil). Because of that, the fractionation could be easily performed with a goal to concentrate the α-pinene even the boiling points of these compounds are very close to each other.

During the fractional distillation at 8.0 kPa, and furthermore at 3.35 kPa, the several fractions were

Table 1. The composition of essential oil of Juniper communis L. used in this study

R_t / min	Component	Content, mass%
14.7	α-Pinene	40.5
16.6	Sabinene	18.0
17.9	Myrcene	13.5
19.2	p-Cymene	2.3
19.9	Limonene	5.1
21.4	γ-Terpinene	2.2
23.1	Terpinolene	1.2
29.4	1-Terpinen-4-ol	2.5
43.5	α-Cubebene	1.0
45.2	α-Copaene	1.4
47.3	β-Elemene	1.1
49.9	β-Cariofilene	0.6
50.8	α-Hymulene	0.6
51.5	Germacrene-D	0.1
53.6	Bicyclogermacrene	1.3
58.2	γ-Cadinene	0.6
58.9	δ-Cadinene	0.6
	Total indentified	91.4

185

Table 2. The procedure of fraction distillation in a laboratory

Fraction	Volume of fraction, cm³	Mass of fraction, g	Temperature (top), °C		Temperature (bottom), °C		Time
			Start	End	Start	End	
Pressure 8 kPa							
1	21	17.8	<40.0	49.0	83.0	85.0	7
2	20	17.0	49.0	59.0	85.0	91.0	15.55
3	20	17.3	59.0	59.0	91.0	91.5	28.52
4	20	17.1	64.0	64.0	94.0	94.0	39.72
5	23	19.0	64.0	64.0	95.5	96.0	53.85
6	23	18.7	64.0	64.5	96.0	100.2	68.78
Sum 1-6	124	106.9	<40.0	66.2	83.0	100.2	68.78
7	22	17.5	66.2	66.2	102.0	104.2	82.65
8	19	15.7	66.0	67.0	105.5	107.5	98.25
9	23	19.6	67.0	67.0	108.0	117.0	123.25
Sum 7-9	64	52.8	66.2	66.8	102.0	117.0	123.25
Pressure 3.35kPa							
10	9.0	6.6	47.0	47.8	121.0	127.0	136.22
11	10.0	7.3	47.4	48.0	129.0	131.5	152.22
12	10.0	7.1	46.8	47.6	134.5	137.5	171.20
13	10.0	6.8	47.5	47.8	139.0	141.0	206.03
14	10.0	6.9	48.0	50.0	146.0	148.8	235.95
Sum 10-14	49.0	34.7	47.0	50.0	121.0	146.0	235.95

collected (14 fractions, Table 3). In the first six fractions the α-pinene was separated with the concentration of more than 98.3 mass%. The next several fractions (7-10) the concentration of α-pinene significantly decrease while sabinene appeared up to the concentration of 42.7. Myrcen and limonene was collected in the next fractions (sum 10-14, Table 3). Such a distribution of the main constituents of juniper berries' essential oil in the fractions was expected, due to the similar boiling temperatures of these chemical compounds (α-pinene 155-156 °C sabinene 163-164 °C, myrcene 167-171 °C, limonene 175-177 °C). According to the present result it is evident that the separation of essential oil by batch vacuum distillation could give the fraction with pure (>99 mass%) α-pinene, as well as fraction with a higher content of sabinene and myrcene. The fractionation of less volatile compounds is not possible because of high temperature in a still pot and thermal degradation of remaining compounds.

Simulation of Juniper's essential oil fractionation

The simulation of batch vacuum distillation was performed using ASPEN Plus® v2006 software. The procedure of critical parameters, as well as the vapour pressure data calculation using the group contribution method for some components of essential oil [16,17] was done; they are presented in Table 4 (M, molecular weight; t_B, normal boiling point; V_B, liquid

volume at t_B; T_C, critical temperature; p_C, critical pressure; v_C, liquid molar volume at critical point; ω - acentric factor; Z_C - compressibility factor). The different group contribution parameters, as well as the calculation procedure for all physical and thermodynamic parameters are previously reported [16-18].

The vapour pressure data (p_V) were calculated using the extended Antoine vapour pressure (p_V in N/m²) equation:

$$\ln p_V = A + B/(T + C) + D*T + E*\ln T + F*T^G$$

where t is temperature in K, and A, B, C, D, E, F and G are coefficients different for every components. They are used from Aspen data base or calculated using the Riedel method [19] enabling the determination of the vapour pressure for the temperature between 200 and 1000 K (Table 5).

Peng Robinson EOS as a thermodynamic model was used for the determination of the vapour-liquid equilibrium composition. The flowsheet of batch distillation (fractionation) column is shown in Figure 2.

The Aspen simulation of juniper berries' essential oil fractional distillation was performed at the same column specification as well as operating conditions, as previously described experiment. The used chemical composition for the input were: 41 mass% of α-pinene, 20 mass% of sabinene, 15 mass% of myrcene, 8 mass% of D-limonene, 5 mass% of γ-terpinene, 5 mass% of terpinen-4-ol and 5 mass% of ger-

macrene. The simulation was performed in three operating steps (periods) in accordance with the experimental data; the first operating step represent the sum of fractions 1-6, the second represent the sum of 7-9 fractions, and the third, the sum of 10-14 fractions. Simulated end time of the first operating step (targeting to the <99mass% α-pinene purity in distillate) was after 74 min when 100.6 °C was reached (Figure 3), what is in good agreement with experimental data (68.3 min and 100.6 °C, Table 3). The yield of this fraction determined by simulation was 115 g what is very close to the experimentally collected mass (Table 3, 106.9 g is sum of 1-6 fractions).

The obtained results indicated that simulation of the distillation process performed by Aspen software, which mainly depends on the proposed thermodynamic model and defined so called "pseudo" mixture

Table 3. The chemical composition of the obtained fractions

Fraction	Composition in fractions, mass %			
	α-Pinene	Sabinene	Myrcene	Limonene
1	99.8	-	-	-
2	99.1	0.4	-	-
3	99.3	0.5	-	-
4	99.0	0.8	-	-
5	98.3	1.5	-	-
6	94.4	5.4	-	-
Sum 1-6	98.3	1.7	-	-
7	86.7	12.8	-	-
8	63.1	35.7	-	-
9	21.9	74.9	2.4	-
Sum 7-9	55.8	42.7	0.9	-
10	1.3	54.4	31.1	11.4
11	0.9	37.3	43.3	17.1
12	0.7	45.0	26.8	25.8
13	-	25.4	39.9	33.1
14	-	12.0	24.0	52.4
Sum 10-14	0.6	36.1	34.3	29.0

Table 4. The physical and thermodynamic parameters for some components present in essential oil (literature and calculated data)

Parameter	α-Pinene	Sabinene	Myrcene	D-limonene	γ-Terpinene	Terpinen-4-ol	Germacrene
M, g/mol	136.24	136.24	136.24	136.24	136.24	136.24	204.36
t_B, °C	156.14	164.04	171.15	177.45	183.00	187.00	308.10
v_B, m^3/kmol	0.1826	0.1845	0.1899	0.1906	0.1942	0.1904	0.3298
T_C, K	644.00	643.00	649.00	653.00	661.00	667.00	804.50
p_C, bar	27.60	27.60	28.00	28.20	28.00	28.20	19.42
v_C, m^3/kmol	0.454	0.494	0.489	0.470	0.489	0.493	0.727
ω	0.221	0.325	0.372	0.381	0.376	0.376	0.437
Z_C	0.234	0.255	0.254	0.244	0.249	0.251	0.211

Table 5. The values of constants used for vapour pressure calculation

Constant	α-Pinene	Sabinene	Myrcene	D-limonene	γ-Terpinene	Terpinen-4-ol	Germacrene
A	97.75	73.81	67.36	91.50	75.57	64.70	72.60
B	-8491.60	-7756.10	-7924.40	-8620.50	-8079.70	-7864.70	-10211.58
C	0.00	0.00	0.00	0.00	0.00	0.00	0.00
D	0.00	0.00	0.00	0.00	0.00	0.00	0.00
E	-11.12	-7.34	-6.29	-10.11	-7.56	-5.89	-6.84
F	5.33E-06	8.04E-18	3.68E-18	4.97E-06	8.39E-18	2.72E-18	1.30E-18
G	2.00	6.00	6.00	2.00	6.00	6.00	6.00

containing only 7 compounds which represents the essential oil well fits the experimental data. Furthermore, this simulation could be used for the optimisation of vacuum distillation of juniper essential oil taking into account different operating condition (number of plate, reflux ratio) and calculating the energy consumption necessary for the realization of a desired separation.
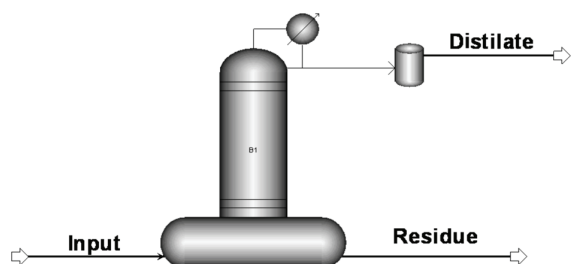

Figure 2. The flowsheet of the batch distillation process.

The analysis of the relation between the number of theoretical plates and the yield of fraction 1 containing more than 99 mass% of α-pinene is shown in Figure 4 and Table 6. One can conclude that a decrease in the number of theoretical plates in a column decreases the yield of fraction 1, as well as the operation time and energy consumption (Figure 4). The isolation of fraction with more than 99 mass% of α-pinene is not possible in a column containing less than 6 theoretical and using reflux ratio 5.

The results of the simulation analysis for different reflux ratio and number of theoretical plates and for fixed composition (purity) of fraction 1 are shown in Table 6.

A detailed calculation performed using a different number of theoretical plates showed that the same energy is consumed per 1 kg of distillate for the same reflux ratio. For example, for reflux ratio 5 and 25, 36 or 45 number of theoretical plates consumed energy is 53.9 MJ (app. 15 kWh), 58.2 MJ (16.2 kWh) and 60.3 MJ (16.8 kWh) for the distillation performed with batch containing 100 kg of juniper essential oil, respectively. Knowing that the market price of juniper essential oil is between 100 and 150 Euros and that it depends on the quality of oil, while the price of energy is about 0.1 Euro/kWh, it seems that the consumed energy in all investigated cases expressed in Euros could be neglected.

According to the results shown in Table 6 and taking into consideration the yield of α-pinene which might be separated from one batch, it is clear that the optimal reflux ratio for a column with 25, 36 or 45 theoretical plates should be 5. Namely, the increase of α-pinene yield is the largest if the reflux ratio increases from 2 to 5; a further increase of the reflux ratio from 5 to 7 and 10 only increases the yield of α-pinene for 10% ($N = 25$) or less ($N = 35$ and $N = 45$).

Process economy

The effect of the separation process depends on the number of plates and reflux ratio and it could be better analyzed if the preliminary or short-cut economic analysis is taken in consideration. The following function based on the mass and energy balance was used for defining the money flow for the separation of one batch:
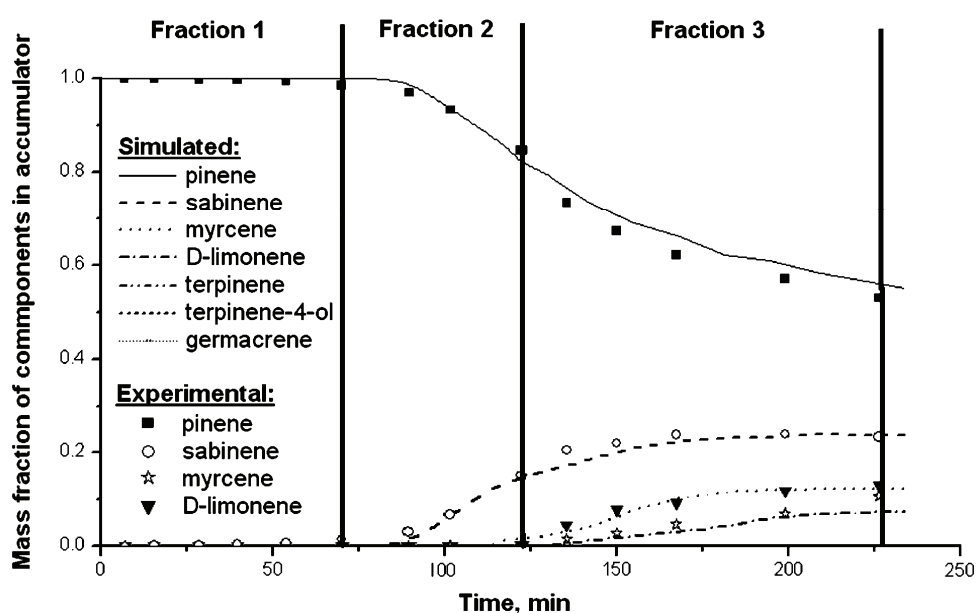

Figure 3. The composition profile during the distillation process.

$$EO(\text{kg}) \times C_1(\frac{\text{euro}}{\text{kg}}) + Energy(\text{kJ}) \times C_2(\frac{\text{euro}}{\text{kJ}}) = Distillate(\text{kg}) \times C_3(\frac{\text{euro}}{\text{kg}}) + residue(\text{kg}) \times C_4(\frac{\text{euro}}{\text{kg}})$$

$C_3 = n \times C_1$

Distillate(kg) $= Y \times EO(\text{kg})$

where: EO - mass of one batch of the essential oil; C_1, C_3 and C_4 are the prices of the essential oil, the α-pinene fraction (distillate) and residue (per 1 kg), and

C_2 the price of energy.

Also, a few assumptions were taken in economic analysis: the value of the residue is set to zero;
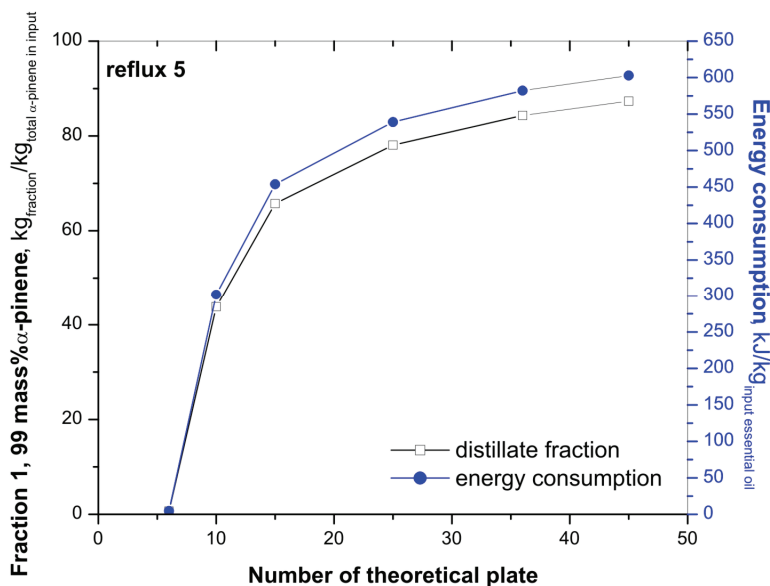
$$C_1(\frac{\text{euro}}{\text{kg}}) = 150 ;$$

Figure 4. The impact of the number of the theoretical plate.

Table 6. The impact of reflux and the number of theoretical stages to distillate the amount and energy consumption for 1 kg charge of juniper essential oil

Parameter	reflux 2	reflux 5	reflux 7	reflux 10
25 Theoretical stages				
Time, min	35.7	76.8	83.4	87.3
Distillate yield[a], kg$_{distillate}$/kg$_{input}$	0.149	0.320	0.348	0.364
Bottom temperature, °C	87.3	92.7	93.9	94.7
Heat duty in reboiler, W	58.4	116.9	155.7	213.8
Consumed energy, kJ/kg$_{distillate}$	839.5	1683.4	2238.9	3076.6
36 Theoretical stages				
Time, min	50.8	83.0	87.4	89.8
Distillate, kg$_{distillate}$/kg$_{input}$	0.211	0.346	0.364	0.374
Bottom temperature, °C	89.2	94.3	95.3	95.9
Heat duty in reboiler, W	58.5	116.9	155.6	213.7
Consumed energy, kJ/kg$_{distillate}$	845.1	1682.5	2241.7	3078.6
45 Theoretical stages				
Time, min	60.2	86.0	89.2	90.8
Distillate, kg$_{distillate}$/kg$_{input}$	0.251	0.358	0.372	0.378
Bottom temperature, °C	90.7	95.4	96.2	96.7
Heat duty in reboiler, W	58.6	116.9	155.6	213.7
Consumed energy, kJ/kg$_{distillate}$	843.3	1684.9	2238.6	3080.0

[a] >99 mass% α-pinene

$$C_2(\frac{euro}{kJ}) = 1.94 \times 10^{-5};$$

the minimum price of α-pinene (distillate) C_3 should be 366 Euro/kg requiring that the cash flow per one batch is not negative; $n = 2.93$ derived from the assumption that 20% income could be realized for theoretical separation of α-pinene present in juniper essential oil.

Solving the equation of the money flow showed that the yield of distillate, Y, should not be lower than 0.341.

The most important conclusion derived from the performed economic analysis showed that the energy consumption has no influence on the process profitability (because of low energy price).

The time necessary for one batch treatment is very important and determines, together with non-productivity time for one batch, how many batches per day might be separated. As it could be seen from the data given in Table 6, the time necessary for separating one batch is not significantly changed for a column with 25, 36 and 45 theoretical stages for all defined profitable distillate yield ($Y \geq 0.341$).

Furthermore, knowing that the smallest investment is for constructing a column with 25 theoretical stages, it seems that the most profitable case will be the separation of juniper essential oil and α-pinene isolation (>99 mass%) in a column with 25 theoretical stages using reflux 7 or more.

CONCLUSION

The fractional separation of juniper essential oil was performed in a vacuum distillation column with 36 stages. Several fractions of distillate were collected and their compositions were analyzed. The obtained results showed that the separation of the essential oil under vacuum could be used for different fractions isolation. The most interesting and important is the first distillate containing α-pinene (> 99 mass%).

The simulation of the batch vacuum distillation process was performed using Aspen software on the basis of a specified thermodynamic model, determined composition of "pseudo" components representing the composition of the essential oil. This model fits the experimental data well (the temperature and composition of collected fractions, their masses and time of distillation). The defined model and simulation procedure were used for the process optimisation and determining the best condition for separating juniper essential oil and α-pinene isolation. Taking into account the prices of essential oil and distillate (α-pinene; >99mass%), the yield of distillate in different column with 25, 36 and 45 theoretical stages,

and under different operating condition (reflux ratio), as well as consumed energy necessary for realizing the distillation process, it was shown that column with 25 theoretical stages with reflux 7 or more gave the most profitable separation of α-pinene (>99 mass%) from juniper essential oil.

REFERENCES

[1] S.B. Glišić, S.Ž. Milojević, S.I. Dimitrijević, A.M. Orlović, D.U. Skala, J. Serb. Chem. Soc., **72** (4) (2007) 311-320

[2] M.Z. Stanković, V.B. Veljković, M. Lazić, Bioactive products of juniper fruit *(Juniperus communis* L.), Monography, Faculty of Technology in Leskovac, University of Niš, 1994 (in Serbian)

[3] B.M. Damnjanović, M.Sc. Thesis, Faculty of Technology and Metallurgy, Belgrade, 2000 (in Serbian)

[4] B. Barjaktarević, M. Sovilj, Z. Knez, J. Agric. Food. Chem. **53** (2005) 2630-2636

[5] L. Janku, U. Hava, O. Motl, Experientia **13** (1957) 255-256

[6] M. Mori, J. Cosm. Derm. **1** (2002) 183-187

[7] B. Tepe, D. Daferera, A. Sokmen, M. Sokmen, M. Polissiou, Food Chem. **90** (3) (2005) 333-340

[8] B. Marongiu, S. Porcedda, A. Caredda, B. de Gioannis, L. Vargiu, P. la Colla, Flavour Fragrance J. **18** (5) (2003) 390-397

[9] T. Fang, M. Goto, M. Sasaki, T. Hirose, J. Agric. Food Chem. **52** (2004) 5162-5167

[10] D. Lopes, A. Raga, G.R. Stuart, J.V. de Oliveira, J. Essent. Oil Res. **15** (2003) 408-411

[11] G.R. Stuart, D. Lopes, J.V. Oliveira, J. Amer. Oil Chem. Soc. **78** (2001) 1041-1044

[12] S. Glisic, Fractionation of *Juniper communis* L. essential oil, Diploma work, Faculty of Technology and Metallurgy, Belgrade, Serbia, 2003 (in Serbian)

[13] Yugoslav standard, 1994, Essential oil analysed with gas chromatography on a capilary column, JUS ISO 7609, Službeni list SRJ, No. 27/94

[14] Yugoslav standard, 1996, Essential oil of juniper (*Juniperus communis* Linnaeus), JUS H. H9. 055, Službeni list SRJ, No. 1/96 (in Serbian)

[15] B.M. Damjanović, D.U. Skala, D.M. Petrović-Đakov, J.K. Baras, J. Essent. Oil Res. **15** (2) (2003) 90-92

[16] R. Gani, L. Constantinou, Fluid Phase Equilibria **116** (1996) 75-86

[17] R. Gani, B. Nielsen, A. Fredenslund, AIChE J. **37** (1991) 1318-1332

[18] S.B. Glišić, D.U. Skala, J. Supercrit. Fluids, 2010, in Press, doi:10.1016/j.supflu.2010.03.005

[19] ASPEN Plus 11.1, Aspen Physical Property System. Methods and Models 11.1.3-32.

SVETOMIR Ž. MILOJEVIĆ[1]
SANDRA B. GLIŠIĆ[2]
DEJAN U. SKALA[2]

[1]Fakultet tehničkih nauka, Kosovska Mitrovica
[2]Katedra za organsko hemijsku tehnologiju, Tehnološko metalurški fakultet, Univerzitet u Beogradu, Beograd

NAUČNI RAD

FRAKCIONA DESTILACIJA ETARSKOG ULJA *Juniperus communis* L.: LABORATORIJSKA ISPITIVANJA, MATEMATIČKA SIMULACIJA I EKONOMIKA PROCESA

U ovom radu je ispitivana separacija etarskog ulja iz bobica kleke (Juniperus communis L. sa podneblja južne Srbije) postupkom šaržne vakuum destilacije. Glavni cilj laboratorijskih ispitivanja je usmeren ka izdvajanju pojedinih frakcija iz etarskog ulja kleke koje sadrže u većem procentu α-pinen, sabinen i mircen, a čine 65 mas% etarskog ulja dobijenog hidrodestilacijom bobica kleke. Rezultati eksperimentalnih ispitivanja sprovedenih šaržnom destilacijom pod vakuumom (8,0-3,35 kPa) u koloni sa 36 teorijskih podova su bili osnova za definisanje odgovarajućeg matematičkog modela i njegovog rešavanja primenom softverskog paketa Aspen. Dobijeno je dobro slaganje između eksperimentalnih vrednosti i vrednosti izračunatih na osnovu ovog modela. Potvrđena korektnost modela iskorišćena je za analizu uticaja različitih operativnih parametara (refluksni odnos od 2 do 10) i konstrukcionih karakteristika kolone (broj podova: 25, 36 i 45) na efekte separacije etarskog ulja kleke. Rezultati su pokazali, na osnovu analize uticaja cene ulazne sirovine, cene izdvojenih frakcija (α-pinen; smeše α-pinena sabinena, mircena) i ukupno utrošene energije za separaciju, da je u laboratorijskim uslovima izvedeno frakcionisanje etarskog ulja kleke najprihvatljivije.

Ključne reči: vakuum frakcionisanje; etarsko ulje Juniper communis L.; α-pinen, Aspen simulacija.